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Dye reorientation in freestanding polystyrene films exhibits fast and slow subpopulations KEEWOOK PAENG, HAU-NAN LEE¹, STEPHEN SWALLEN, MARK EDIGER, University of Wisconsin-Madison — The segmental dynamics of freestanding polystyrene films as thin as 14 nm were studied by measuring the reorientation of dilute dye molecules. Both temperature ramping and isothermal anisotropy measurements reveal the existence of two subsets of dye molecules with differing dynamics. The dynamics of the slow subset matches the dynamics observed in thick films. The reorientation time scale of the fast subset is a few hundred seconds at Tg-25 K and has weak temperature dependence. At Tg- 5 K, the average relaxation time of these two subsets differs by 4 orders of magnitude. The fraction of the sample with fast dynamics increases with temperature and does not depend on the molecular weight of the polymer. We interpret the fast subset as a mobile surface layer and estimate a thickness of 6 nm at the bulk Tg.

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